

# A Wannier-function-based *ab initio* Hartree-Fock study of polyethylene

Alok Shukla<sup>†</sup>, Michael Dolg

*Max-Planck-Institut für Physik komplexer Systeme, Nöthnitzer Straße 38 D-01187 Dresden,  
Germany*

Hermann Stoll

*Institut für Theoretische Chemie, Universität Stuttgart, D-70550 Stuttgart, Germany*

## Abstract

In the present letter, we report the extension of our Wannier-function-based *ab initio* Hartree-Fock approach—meant originally for three-dimensional crystalline insulators—to deal with quasi-one-dimensional periodic systems such as polymers. The system studied is all-*transoid* polyethylene, and results on optimized lattice parameters, cohesive energy and the band structure utilizing 6-31G\*\* basis sets are presented. Our results are also shown to be in excellent agreement with those obtained with traditional Bloch-orbital-based approaches.

## 1. INTRODUCTION

Polyethylene, with its rather simple geometric and electronic structure, can be characterized as a prototype of all insulating polymers. Perhaps for that reason, and certainly because of its technological importance, it is one of the most extensively studied systems, both experimentally, and theoretically. Its geometrical structure has been investigated in a number of experiments both by x-ray diffraction techniques [1–3], and by the neutron-scattering method [4]. The electronic structure of polyethylene has been investigated in photoconduction and photoemission experiments resulting in the determination of its band gap [5], and in angle-resolved photoemission experiments leading to the measurement of its valence-band structure [6]. Theoretically it has been investigated by a number of semiempirical methods [7–11], by the *ab initio* crystal-orbital Hartree-Fock (HF) method [12–16], and by subsequent many-body perturbation theory (MBPT) based correlation methods [17–19]. Correlation effects have also been accounted for in studies using density-functional theory [20–23].

Recently we have proposed an approach to study the electronic structure of periodic insulators in terms of Wannier functions [24], with the long-term goal of a wavefunction-based treatment of electron correlation effects in three-dimensional (3D) crystalline solids. The approach has been made much more efficient as compared to its original implementation, and has since been applied, at the HF level, to study the electronic structure, and various related properties, of a variety of 3D ionic insulators [25–27]. As a further improvement of the approach, we have extended it to deal with quasi-one-dimensional (1D) periodic systems such as polymers, as demonstrated in the present letter by means of an all-electron study of all-*transoid* polyethylene. The details of the approach pertaining to its implementation, along with its applications to an infinite LiH chain and all-*trans* polyacetylene, are reported elsewhere [28].

As is evident from the results of refs. [17–19], impressive successes can be achieved in the *ab initio* treatment of electron-correlation effects for the case of 1D systems such as polymers, even within Bloch-orbital-based approaches. However, generalization to a 3D solid is far from trivial because, for such a system, owing to the higher dimensionality of its Brillouin zone, the sum over the virtual states in the k-space will involve a huge number of terms. Moreover, the larger degree of degeneracy generally associated with Bloch orbitals of a 3D crystal (band crossing), will make such an approach even more difficult to implement. This is the reason behind our belief that Wannier functions offer the most natural language, in which to formulate the *ab initio* treatment of electron-correlation effects, as their utility is not restricted to systems of any particular dimensionality. And which electrons will contribute to important correlation effects can be decided almost intuitively, as electrons localized on Wannier functions which are far-apart, will interact only weakly. However, being a relatively new approach, it is important for us to check its applicability on a variety of systems even at the HF level. Since a large body of high-quality theoretical and experimental data already exists on polyethylene, any new theoretical study of the compound can be judged against it. This is the reason that we present a HF study of all-*transoid* polyethylene in the present letter, utilizing the, relatively large, 6-31G\*\* basis set employing polarization functions. In order to be absolutely certain about the correctness of our method, we also used the Bloch-orbital-based CRYSTAL program [29] to study the same compound employing the

identical 6-31G\*\* basis set, and those results are also presented for comparison. We note that Wannier functions have been employed in earlier *ab initio* studies of electron correlation effects in polymers [30]. However, unlike the past studies where the Wannier functions were obtained by localizing the Bloch orbitals, the present work leads to direct determination of Wannier functions of the polymers, without invoking the Bloch orbitals.

The remainder of the paper is organized as follows. In Section 2, we briefly describe the theory with particular emphasis on the treatment of the Coulomb lattice sums which differs from the Ewald-summation based approach adopted for our earlier studies on 3D crystals. In section 3, we present the results of our calculations which include optimized geometry, cohesive energy, band structure, and contour plots of some of the Wannier functions. Finally, section 4 contains our conclusions.

## 2. THEORY

In our previous papers [24,25] we showed that, for a crystalline insulator with  $2n_c$  electrons per unit cell, one can obtain its  $n_c$  restricted-Hartree-Fock(RHF) Wannier functions localized in the reference unit cell,  $\{|\alpha\rangle; \alpha = 1, n_c\}$ , by solving the equation

$$(T + U + \sum_{\beta} (2J_{\beta} - K_{\beta}) + \sum_{k \in \mathcal{N}} \sum_{\gamma} \lambda_{\gamma}^k |\gamma(\mathbf{R}_k)\rangle \langle \gamma(\mathbf{R}_k)|) |\alpha\rangle = \epsilon_{\alpha} |\alpha\rangle, \quad (1)$$

where  $T$  represents the kinetic-energy operator,  $U$  represents the interaction of the electrons of reference cell with the nuclei of the whole of the crystal while  $J_{\beta}$ ,  $K_{\beta}$  are the Coulomb and the exchange operators defined as

$$\left. \begin{aligned} J_{\beta} |\alpha\rangle &= \sum_j \langle \beta(\mathbf{R}_j) | \frac{1}{r_{12}} | \beta(\mathbf{R}_j) \rangle |\alpha\rangle \\ K_{\beta} |\alpha\rangle &= \sum_j \langle \beta(\mathbf{R}_j) | \frac{1}{r_{12}} | \alpha \rangle | \beta(\mathbf{R}_j) \rangle \end{aligned} \right\}, \quad (2)$$

The first three terms of Eq.(1) constitute the canonical Hartree-Fock operator, while the last term is a projection operator which makes the orbitals localized in the reference cell orthogonal to those localized in the unit cells in the immediate neighborhood of the reference cell, in the limit of infinitely high shift parameters  $\lambda_{\gamma}^k$ 's. These neighborhood unit cells, whose origins are labeled by lattice vectors  $\mathbf{R}_k$ , collectively define an “orthogonality region” and are denoted by  $\mathcal{N}$ . The projection operators along with the shift parameters play the role of a localizing potential in the Fock matrix, and once self-consistency has been achieved, the occupied eigenvectors of Eq.(1) are localized in the reference cell, and are orthogonal to the orbitals of  $\mathcal{N}$ —thus making them Wannier functions [24,25]. The size of  $\mathcal{N}$  can be denoted by specifying the number  $N$  of nearest neighbors that are included in  $\mathcal{N}$ . For example,  $N = 3$  shall imply that  $\mathcal{N}$  contains up to third-nearest neighbors of the reference cell, and so on. From the Wannier functions localized in the reference cell (cf. Eq. (1)) one can obtain the corresponding orbitals localized in any other unit cell by the expression

$$|\alpha(\mathbf{R}_i)\rangle = \mathcal{T}(\mathbf{R}_i) |\alpha(0)\rangle, \quad (3)$$

where  $|\alpha(0)\rangle$  represents a Wannier orbital localized in the reference unit cell assumed to be located at the origin while  $|\alpha(\mathbf{R}_i)\rangle$  is the corresponding orbital of the  $i$ -th unit cell located

at lattice vector  $\mathbf{R}_i$ , and the corresponding translation is induced by the operator  $\mathcal{T}(\mathbf{R}_i)$ . Thus Eqs. (1) and (3) provide us with the complete HF solution of the infinite crystal.

We have computer implemented the approach outlined above within a linear-combination of atomic orbital (LCAO) approach, utilizing Gaussian lobe-type basis functions [31]. The nontrivial aspect of the program mainly involves the evaluation of the infinite lattice sums contained on the right hand side of Eq. (2). The evaluation of exchange lattice sums can be performed entirely in the real-space for insulators quite inexpensively, utilizing the rapidly decaying nature of both the lattice sums, as well as that of the single-particle density matrix. However, the Coulomb lattice sums are divergent on their own. The contribution of the Coulomb interaction to the Fock matrix converges only when the electron-repulsion lattice sums are appropriately combined with the lattice sums involving electron-nucleus attraction. For the 3D systems studied earlier, we used an Ewald-summation based approach to perform the lattice sums involved in the Coulomb series [24–27]. However, for the treatment of quasi 1D systems such as polymers, we have adopted an entirely real-space based approach towards the evaluation of the Coulomb series, the details of which have been presented elsewhere [28]. For the sake of completeness we will briefly outline the salient features of the approach here as well. In this approach, all the matrix elements needed to represent the canonical HF operator included in Eq. (1) in the LCAO form can be generated from the translationally invariant skeleton of the corresponding Fock matrix [28]

$$\begin{aligned}
F_{pq}(\mathbf{t}_{pq}) = & \langle p(\mathbf{t}_{pq}) | T | q(0) \rangle - \sum_{j=-M}^M \sum_A^{\text{atoms}} \langle p(\mathbf{t}_{pq}) | \frac{Z_A}{|\mathbf{r} - \mathbf{R}_j - \mathbf{r}_A|} | q(0) \rangle \\
& + 2 \sum_{j=-M}^M \sum_{r,s} \sum_{\mathbf{t}_{rs}} \langle p(\mathbf{t}_{pq}) | r(\mathbf{t}_{rs} + \mathbf{R}_j) | \frac{1}{r_{12}} | q(0) s(\mathbf{R}_j) \rangle D_{rs}(\mathbf{t}_{rs}) \\
& - \sum_k \sum_{r,s} \sum_{\mathbf{t}_{rs}} \langle p(\mathbf{t}_{pq}) | s(\mathbf{R}_k) | \frac{1}{r_{12}} | r(\mathbf{t}_{rs} + \mathbf{R}_k) q(0) \rangle D_{rs}(\mathbf{t}_{rs}) . \tag{4}
\end{aligned}$$

The notation used in the equation above is consistent with the one introduced in our earlier work [25] where, e.g.,  $|p(\mathbf{t}_{pq})\rangle$  denotes the  $p$ -th basis function located in the unit cell labeled by lattice vector  $\mathbf{t}_{pq}$  and  $|q(0)\rangle$  denotes the  $q$ -th basis function located in the reference cell. Additionally,  $\mathbf{R}_j$ ,  $\mathbf{R}_k$ ,  $\mathbf{t}_{pq}$ , and  $\mathbf{t}_{rs}$  represent (arbitrary) translation vectors of the lattice, and  $D_{rs}(\mathbf{t}_{rs})$  represents the elements of the one-particle density matrix of the infinite system assuming that  $r$ -th function is located in the cell  $\mathbf{t}_{rs}$  while the  $s$ -th function is in the reference cell. The second and the third elements of the equation represent the electron-nucleus and electron-electron interaction parts of the Coulomb series, respectively. The lattice sums representing both types of contributions to the Coulomb series are denoted by the sums over index  $j$ . The Coulomb contribution to the Fock matrix element displayed above is brought to convergence by choosing to terminate both the lattice sums at the same and a “sufficiently-large” value of the index  $j$ . We choose to denote this value by variable  $M$ , which clearly implies the inclusion of the Coulomb interaction of the reference cell electrons with those in up to its  $M$ -th nearest neighbors. As a consequence of the fact that the unit cell is electrically neutral, the divergences inherent in the two Coulomb contributions are equal and opposite in nature and should cancel themselves for large values of  $M$ . In order to obtain the correct value of the total energy per unit cell, the nucleus-nucleus repulsion energy is also computed by restricting the corresponding sum to  $M$  nearest neighbors of the reference

cell. The last term of Eq. (4) represents the contribution of the exchange interaction. The corresponding lattice sums represented by index  $k$  converge rapidly in the real space with increasing value of  $k$ . The lattice sums corresponding to the cell index  $\mathbf{t}_{rs}$  also converge fast for insulating systems because of the rapidly decaying nature of the corresponding density matrix elements  $D_{rs}(\mathbf{t}_{rs})$ , with increasing value of  $|\mathbf{t}_{rs}|$  [29]. The present, entirely real-space-based approach to the infinite lattice sums is quite common in polymer studies, and can be found in the literature dating back to the seventies. An excellent review of the general real-spaced-based approaches can be found, e.g., in the work of Delhalle et al. [32].

In the theory described above there are two free parameters viz.,  $N$  which represents the size of the orthogonality region of the Wannier functions of the reference cell, and  $M$  which represents the range of the Coulomb interaction included in the Fock matrix. In another paper [28] we have presented a detailed study of the influence of these parameters on the total energy per unit cell for the infinite LiH chain and all-*trans* polyacetylene. In all the cases we found that  $N = 3$  and  $M = 75$  yielded total energies converged up to  $\approx 0.1$  mHartree. In the present study we have used the values  $N = 5$  and  $M = 85$ .

The band structure presented in this work was obtained using the approach outlined in our previous work [26]. This is achieved by performing a Fourier transform on the final converged real-space Fock matrix (cf. Eq. (4)) to obtain its reciprocal-space ( $k$ -space) representation. Then the corresponding Fock matrix is diagonalized at different  $k$  points to obtain the band structure.

### 3. CALCULATIONS AND RESULTS

In this section we present the results of calculations performed on polyethylene in its all-*transoid* geometry. The polymer was modeled as a single chain oriented along the x-axis, as shown in Fig. 1. Since our program is not yet able to utilize the point-group symmetry, the reference unit cell was assumed to consist of a single  $\text{C}_2\text{H}_4$  unit, as against a  $\text{CH}_2$  unit if the use of the point-group symmetry were possible. The bonds included in the reference cell during the calculations are also indicated in Fig. 1. There are four geometrical parameters involved in the structure of all-*transoid* polyethylene namely, carbon-carbon bond length ( $R_{CC}$ ), carbon-carbon-carbon bond angle ( $\alpha$ ), carbon-hydrogen bond length ( $R_{CH}$ ) and hydrogen-carbon-hydrogen bond angle ( $\beta$ ). In the present calculations all four parameters were optimized.

We adopted a 6-31G\*\* basis set, the same basis set which we also used to study all-*trans* polyacetylene in our previous work [28]. The polarization functions used in the basis set consisted of one p-type exponent of  $0.75 \text{ Bohr}^{-2}$  on hydrogen and a single d-type exponent of  $0.55 \text{ Bohr}^{-2}$  on carbon. Thus the basis set on carbon was [3s,2p,1d] type while the one on hydrogen was of [2s,1p] type. In our calculations, of course, we used the lobe representation of the corresponding p- and d-type Cartesian basis functions, while the true Cartesian basis functions were used in the calculations performed with the CRYSTAL program. For the six atoms included in the reference cell the present choice of the basis set amounted to 48 basis functions per unit cell. Since we chose to orthogonalize the Wannier functions of the reference cell to those residing in its up to fifth-nearest neighbor cells, we had to include the basis functions of those cells so as to be able to satisfy the orthogonality condition. This increases the total number of basis functions associated with the reference cell Wannier

functions to 528, which, of course, amounts to an enormous increase in the dimension of the Fock matrix (cf. Eq. (1)) to be diagonalized. However, the integral evaluation time, which dominates the calculations, is unaffected by this proliferation in the basis set size associated with the Wannier functions. The reason for that is that the one- and two-electron integrals are evaluated with full regard to the translational symmetry of the problem [25,28], and therefore depend only on the number of basis functions per unit cell.

Our results on the optimized geometry and the total energy per unit cell along with the corresponding cohesive energy obtained with the 6-31G\*\* basis set are presented in table 1 which also compares them to the calculations performed by us—employing the same basis set—with the CRYSTAL program. As far as the comparison with the works of other authors is concerned, we will restrict it only to calculations in which the *ab initio* crystal HF approach was adopted. To the best of our knowledge, only Karpfen [12] and Teramae et al. [13] have performed full geometry optimization for all-*transoid* polyethylene within an *ab initio* crystal Hartree-Fock approach. These authors, of course, employed a Bloch-orbital-based formalism and their results are also summarized in table 1. Karpfen [12] used both the STO-3G basis set as well as an extended basis set employing a [4s,2p] set for carbon and a [2s] set for hydrogen. Teramae et al. used only the STO-3G set in their calculations. Thus, polarization functions were used in neither of the papers. It is clear from the table that the agreement between the results obtained with our approach, and the ones with the CRYSTAL program, is very close. The agreement between our results and those of other authors is generally satisfactory, i.e., the deviations are within the limits of uncertainties associated with quantum-chemical calculations, except for the carbon-carbon bond length ( $R_{CC}$ ) which is about 0.03 Å shorter than the best values reported by Karpfen [12] and Teramae et al. [13]. A possible reason is the use of polarization functions in our calculations. Experimental results on polyethylene are available from x-ray scattering experiments [1–3] as well as from neutron-scattering experiments [4], and are summarized in table 1. As far as the comparison with the experiments is concerned our results for all parameters, except for the carbon-hydrogen bond length ( $R_{CH}$ ), are in good agreement with the experimental results obtained with the x-ray scattering techniques [1–3].  $R_{CH}$  in the present calculations is overestimated by about 0.03 Å compared to the x-ray scattering results. However, for this parameter, results of other authors also differ by at least that amount. Thus, in our opinion, this discrepancy may be due to electron-correlation effects. We also present results for the cohesive energy per CH<sub>2</sub> unit obtained from ours as well as CRYSTAL calculations. For that purpose we used Hartree-Fock reference energies for carbon and hydrogen of -37.677838 a.u. and -0.498233 a.u., respectively. These energies were obtained by performing atomic HF calculations employing the same 6-31G basis set as used in the polymer calculations. Our results for the cohesive energy are in excellent agreement with the one obtained with the CRYSTAL program, however, we could not locate any other theoretical or experimental results on the cohesive energy of polyethylene.

In Fig. 2 we present the band structure of all-*transoid* polyethylene computed with the 6-31G\*\* basis set determined by our approach as well as the one computed using the CRYSTAL program. Although, in what follows, we have not compared our HF band structure with those presented in the works of other authors [12,14], even a cursory comparison reveals that the qualitative features of all the Hartree-Fock energy bands are essentially the same. Our band structure was computed with  $N = 5$  and  $M = 100$  while in the CRYSTAL

calculations one hundred  $k$  points were used to perform the integration over the Brillouin zone [29]. Since our results for the geometry were in better agreement with the experimental one determined with the x-ray scattering techniques, we chose to evaluate the band structure for the corresponding geometrical parameters [1–3]. Six highest occupied bands along with the seven lowest unoccupied bands are presented in Fig. 2. The absolute values of the band energies naturally differed somewhat owing to the different treatment of the Coulomb series in the two approaches. Therefore we shifted all the CRYSTAL band energies so that the tops of the valence bands obtained from the two sets of calculations coincided. Clearly the agreement between our band structure and the one obtained with the CRYSTAL program is very good. The value of the direct band gap (at  $k = 0$  point) is 0.6088 a.u. (16.57 eV) obtained with our approach is in excellent agreement with the corresponding CRYSTAL value of 0.6077 a.u. (16.54 eV). We believe that the small differences between our band structure and the one computed using the CRYSTAL program are mainly due to the use of lobe functions in our approach to approximate the Cartesian basis functions used by the CRYSTAL program. The value of the direct gap for all-*transoid* polyethylene was measured to be 8.8 eV by Less et al. [5]. Therefore, as is generally the case with HF bands, the band gap of polyethylene is overestimated by a factor of two, pointing to the importance of the electron correlation effects. With our approach the highest point of the valence band occurs at  $\approx 10.46$  eV which, according to the Koopmans theorem, can be directly compared to the ionization potential of the compound. The experimental value of the ionization potential of polyethylene is reported to be in the range 9.6–9.8 eV [6]. Although the agreement between the HF value and the experimental one is better for the ionization potential as compared to the band gap, the differences still point to the importance of electron-correlation effects. Sun et al. [19] recently studied the influence of electron correlation effects on the valence band of polyethylene using a Bloch-orbital-based second-order many-body perturbation theory. The improvement over the HF results which they observed testifies to the general belief that electron correlation effects are essential to describe the quasi-particle properties in such systems.

One can obtain an intuitive understanding of the chemical bonding in the system by examining the Wannier functions. Such views are presented in Figs. 3 and 4 which display the charge densities of the Wannier functions corresponding to the bonds of the unit cell, which are antisymmetric ( $\pi$ -like) under the reflection about the  $xy$  plane. The contour plots correspond to the charge density associated with the corresponding Wannier function in the  $xy$  plane with  $z = 0.25$  atomic units. These orbitals were evaluated at the experimental geometry used also to compute the band structure. Fig. 3 clearly implies a Wannier function which has a bonding character with respect to the two carbon atoms of the unit cells, while the second  $\pi$ -like shown in Fig. 4 displays an antibonding character. Both the Wannier functions possess bonding characters with respect to the C-H bonds of the unit cell. From the contour plots the localized nature of the orbitals is quite obvious. The  $\sigma$ -type Wannier functions (not presented here), although still localized within the unit cell, are mixtures of both the traditional C-C and the C-H bonds.

#### 4. CONCLUSIONS AND FUTURE DIRECTIONS

In conclusion, an *ab initio* Wannier-function-based Hartree-Fock approach developed originally to treat infinite 3D crystalline systems has been applied to a 1D system, namely, polyethylene. The main difference as compared to the case of 3D systems has been an entirely real-space based treatment of the Coulomb series. The approach yields results which are in excellent agreement with those obtained using the CRYSTAL program, where Ewald summation is used to perform the Coulomb lattice sums. In future, we intend to make our treatment of the Coulomb series more efficient by incorporating real-space multipole expansion techniques.

The discrepancy between our Hartree-Fock results for all-*transoid* polyethylene and the experimental ones was found to be most significant for the band structure. For example, the Hartree-Fock value of the direct band gap is wrong by a factor of two as compared to the experimental one. These differences point to the importance of electron-correlation effects. In a future publication, we will include these within a local-correlation approach to study their influence on the quasi-particle properties of polyethylene and other insulating systems [33,34].



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# FIGURES

A. Shukla et al.: Fig. 1

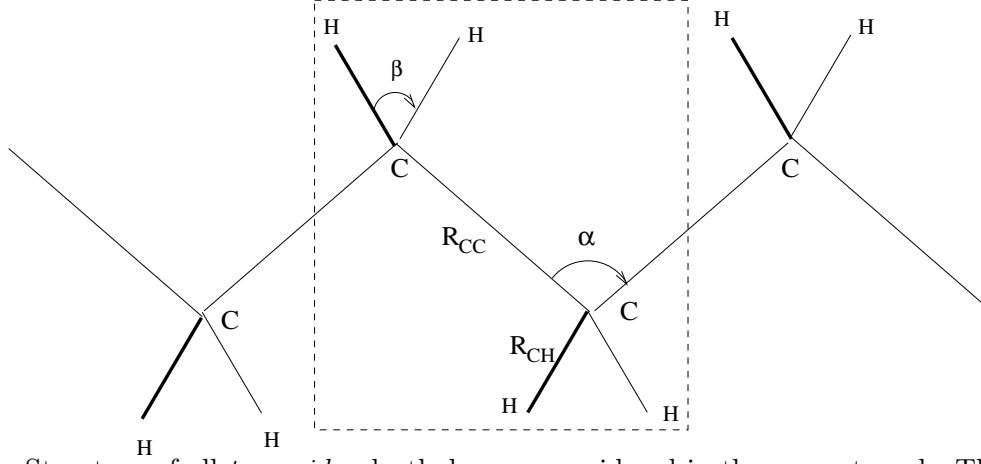


FIG. 1. Structure of all-*transoid* polyethylene as considered in the present work. The polymer is assumed to be oriented along the  $x$  direction. CC bonds are in the  $xy$  plane while the CH bonds are in the  $yz$  plane. Bonds included in the reference cell in the calculations are enclosed in the dashed box; the two CC bonds crossing the borderline are translationally equivalent, and only one of them is included in the reference cell.

A. Shukla et al.: Fig 2

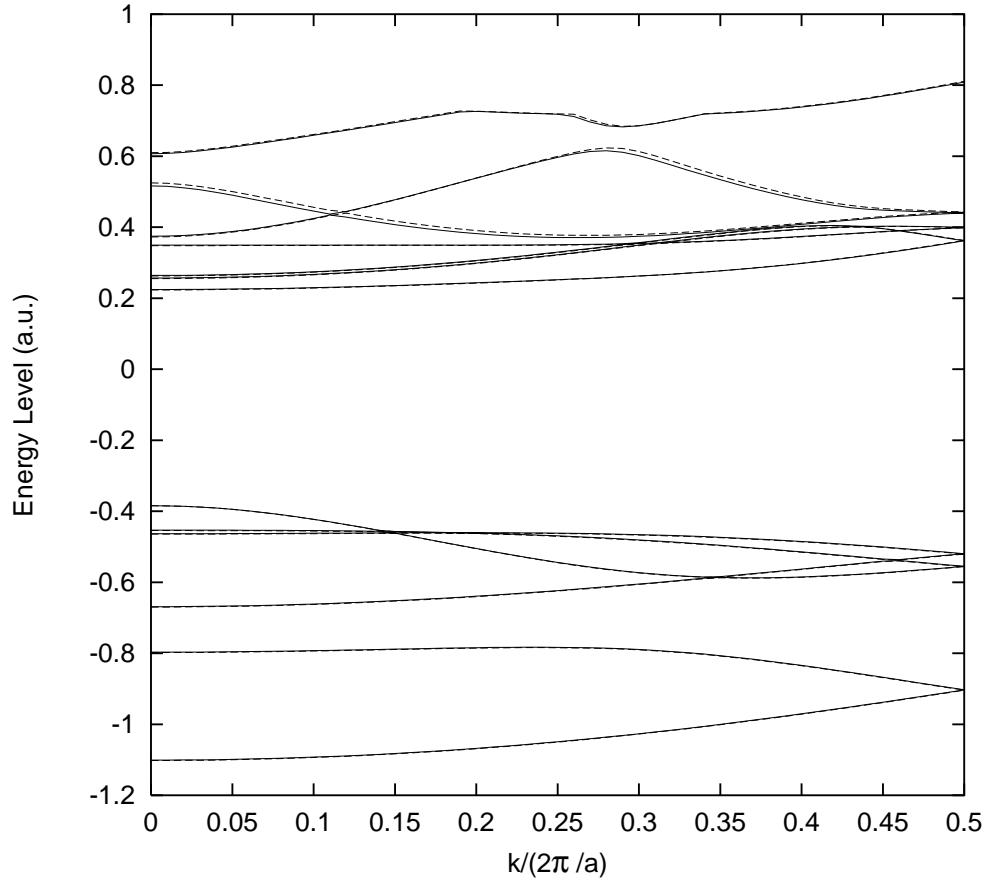


FIG. 2. Band structure of polyethylene obtained using our approach (solid lines) compared to that obtained using the CRYSTAL program (dashed lines). The experimental geometry (x-ray scattering) [1–3] and a 6-31G\*\* basis set were used in both cases. The close agreement between the two sets of bands is obvious.

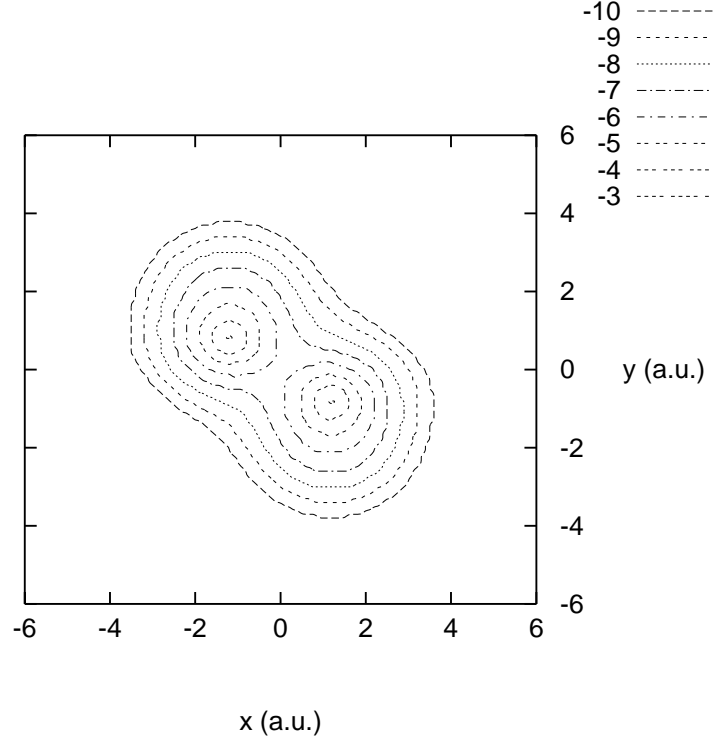


FIG. 3. Contour plots of the charge density of the  $\pi$ -type valence Wannier function of the reference cell. Contours are plotted in the  $xy$  plane with  $z = 0.25$  a.u. ( $x$  is the axis of the polymer). The magnitude of the contours is on a natural logarithmic scale. The two carbon atoms of the unit cell are located at the positions  $(\mp 1.2, \pm 0.81, 0.0)$  a.u., while the four hydrogen atoms are at locations  $(\mp 1.2, \pm 2.01, \pm 1.62)$  a.u., approximately. The orbital clearly has a bonding character with respect to both the carbon-carbon as well as the carbon-hydrogen bond. The rapidly decaying strength of the contours testifies to the localized nature of the Wannier function.

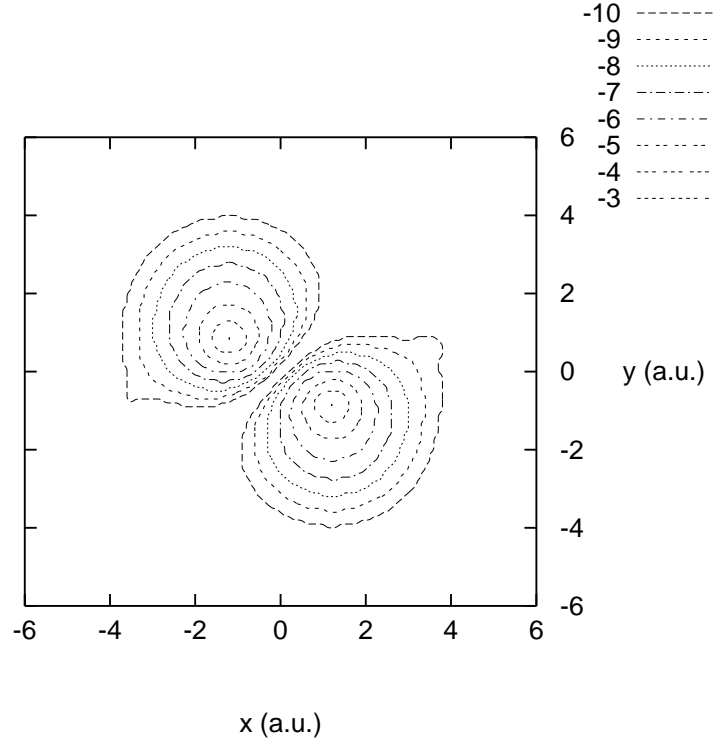


FIG. 4. Contour plots of the charge density of the second  $\pi$ -type valence Wannier function of the reference cell. The geometrical information is same as in the caption of Fig. 3. This contour plot clearly indicates an antibonding character of the Wannier function with respect to the two carbon atoms of the unit cell, and a bonding character with respect to the carbon-hydrogen bonds. Some weaker contours can be seen to reach the carbon atoms belonging to the nearest-neighbor unit cells.

# TABLES

TABLE 1. A summary of our HF results on all-*transoid* polyethylene performed with the 6-31G\*\* basis set and its comparison with the corresponding calculations performed by us with the CRYSTAL program and the HF results of other authors. The Wannier-function-based calculations were performed with up to fifth-nearest neighboring cells included in the orthogonality region ( $N = 5$ ) and eighty five neighbors included in the Coulomb series ( $M = 85$ ). Experimental values are also listed for comparison. The lengths are expressed in the units of Å, the bond angles are in degrees, the total energy per C<sub>2</sub>H<sub>4</sub> unit ( $E_{\text{total}}$ ) is in Hartrees while the cohesive energy per CH<sub>2</sub> unit ( $E_{\text{coh}}$ ) is in eV.

	$R_{CC}$	$R_{CH}$	$\alpha$	$\beta$	$E_{\text{total}}$	$E_{\text{coh}}$
This work <sup>a</sup>	1.532	1.092	113.0	106.6	-78.0728	9.85
CRYSTAL	1.533	1.092	113.2	106.5	-78.0723	9.85
Karpfen <sup>b</sup>	1.562	1.102	112.2	107.4	—	—
Karpfen <sup>c</sup>	1.547	1.089	112.6	107.0	—	—
Teramae et al. <sup>d</sup>	1.565	1.102	115.3	104.7	—	—
Exp. <sup>e</sup>	1.53	1.069	112.0	107.0	—	—
Exp. <sup>f</sup>	1.578	1.06	107.7	109.0	—	—

<sup>a</sup> Performed with the lobe representation of the 6-31G\*\* basis set.

<sup>b</sup> Performed with an extended basis set without polarization functions. Ref. [12]

<sup>c</sup> Performed with the STO-3G basis set. Ref. [12]

<sup>d</sup> Performed with the STO-3G basis set. Ref. [13]

<sup>e</sup> X-ray scattering results at 4 K. Refs. [1–3]

<sup>f</sup> Neutron scattering results at 4 K. Ref. [4]